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FORM PTO-1390 (Modified) (REV 10-95) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER
A-6865

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR
09/446128

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP98/03349	**04 June 1998 (04.06.98)**	**04 July 1997 (04.07.97)**

TITLE OF INVENTION
PROCESS FOR FURTHER PROCESSING OF SMALL GLASS PARTICLES

APPLICANT(S) FOR DO/EO/US
CHRISTIAN KLEPSCH GLASTECHNOLOGIE GMBH

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
    A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☒ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☐ Certificate of Mailing by Express Mail
19. ☐ Other items or information:

"Marked-Up" copy of specification and copy of German application

 PCTUS1/REV03

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U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
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20. The following fees are submitted:.

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

		CALCULATIONS	PTO USE ONLY
☒ Search Report has been prepared by the EPO or JPO	**\$840.00**		
☐ International preliminary examination fee paid to USPTO (37 CFR 1.482)	**\$670.00**		
☐ No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))	**\$760.00**		
☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO	**\$970.00**		
☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)	**\$96.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =		**\$840.00**	
Surcharge of **\$130.00** for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).	☐ 20 ☒ 30	**\$130.00**	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	13 - 20 =	0	x \$18.00	**\$0.00**	
Independent claims	1 - 3 =	0	x \$78.00	**\$0.00**	
Multiple Dependent Claims **(check if applicable).**			☐	**\$0.00**	
TOTAL OF ABOVE CALCULATIONS =				**\$970.00**	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) **(check if applicable).**			☐	**\$0.00**	
SUBTOTAL =				**\$970.00**	
Processing fee of **\$130.00** for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).			☐ 20 ☐ 30 +	**\$0.00**	
TOTAL NATIONAL FEE =				**\$970.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).**			☐	**\$0.00**	
TOTAL FEES ENCLOSED =				**\$970.00**	
				Amount to be: refunded	\$
				charged	\$

☒ A check in the amount of **\$970.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. in the amount of to cover the above fees. A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **08-2455** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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SIGNATURE

Stewart L. Gitler
NAME

31,256
REGISTRATION NUMBER

12/23/99
DATE

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

CHRISTIAN KLEPSCH
GLASTECHNOLOGIE GMBH

Group Art Unit:

Serial No :

Examiner:

Filed :

For : **PROCESS FOR FURTHER PROCESSING OF SMALL GLASS PARTICLES**

PRELIMINARY AMENDMENT

Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

Please amend the above-identified application as follows:

In the Specification:

Please delete the current Specification and replace same with the "Substitute Specification" attached hereto.

In the Claims:

Please delete claims 1-11, and kindly insert in their place claims 12-24, as follows:

--12. A process for further processing of small glass particles, in a form of a scrap glass granulate with a grain size ranging between 0.3 and 4 mm, or glass beads with diameters in the range between 0.1 and 2.3 mm, comprising the steps of contacting surfaces of the small glass particles with a low melting silicate flux, or enamel, selected from lead borosilicate, sodium borosilicate, fluoroborosilicate or mixtures thereof, in amounts of 2 to 9% by weight, and then, exposing the small glass particles to a heat treatment in the range between 540°C and 800°C, whereby the low melting silicate flux or enamel, melts on the surfaces of the glass particles.

13. The process for further processing of small glass particles, as claimed in claim 12, wherein the low melting silicate flux, or enamel, is present in an amount ranging from 3 to 5% by weight.

14. The process for further processing of small glass particles, as claimed in claim 12, wherein the heat is in the range of 540°C to 660°C.

15. The process as claimed in claim 12, wherein the surfaces of the glass particles, before making contact with the silicate flux or enamel, are treated with a wetting agent in the form of an screen printing oil which gasifies without residue, a liquid which contains both boric acid and fluorine salts or mixtures thereof.

16. The process as claimed in claim 12, wherein the low melting silicate flux, or enamel, contains color pigments so that subsequent to the heat treatment, a pulverizing or grinding step occurs wherein small glass particles are formed as a glass granulate or glass beads with a color layer fired onto an outside of the glass particles.

17. The process as claimed in claim 12, wherein the heat treatment is done in an oxidizing or a reducing atmosphere.

18. The process as claimed claim 12, wherein a layer of the low melting silicate flux, or enamel, is applied to one or both surfaces of a flat material, wherein a layer of selectively colored or uncolored glass particles is applied to one or both wetted surfaces of the flat carrier material within a framework of a spraying process, and wherein following a completed rolling process, heat treatment is done in which the formation of securely adhering connecting bridges between the

glass particles among one another and the surface of the flat carrier material occurs.

19. The process as claimed in claim 18, wherein the flat carrier material is a thin flat glass or a flexible glass film.

20. The process as claimed in claim 18, wherein the flat carrier material is made in a form of ceramic tiles.

21. The process as claimed in claim 18, wherein the flat carrier material is a metal surface of a body of a land vehicle, a surface of a ship's hull or an aircraft's surface.

22. The process as claimed in claim 18, wherein the flat carrier material is a fireproof fabric in the form of a looped glass fabric or a ceramic fabric.

23. The process as claimed in claim 12, wherein the glass beads are coated with the low melting silicate flux, or enamel, within a mixing device, whereupon a pasty mass is produced and is placed in a corresponding mold, after which heat treatment porous glass elements are formed in a form of flat plates, relief panels, glass blocks, wall panels, or cladding panels.

24. The process as claimed in claim 12, wherein the small glass particles are coated with the low melting silicate flux, or enamel, within a mixing device, whereupon a pasty mass is produced and is placed in a cavity between two flat glass plates or glass films, after which heat treatment heat insulating glass panes are formed.--

In the Abstract:

Kindly add the Abstract of the Disclosure attached hereto.

REMARKS

Applicant has amended the claims to coincide with U.S. Patent Practice. Multiple dependencies as well as a number of §112 informalities have been addressed. Further, Applicant has submitted a revised specification along with a marked-up copy of the specification and a "Substitute Specification" in an effort to put this application in better condition for review by the U.S. Patent and Trademark Office.

No new matter has been inserted either into the claims or the specification. Any changes have been merely to incorporate wording in the original claims into the specification for clarity.

Further, an Abstract of the Disclosure has been added to the application.

If any questions remain, please feel free to contact the undersigned.

Respectfully submitted,

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Reg. No. 31,256

December 23, 1999
(703)415-0100

Attorney Docket No: **A-6865.PAM/cat**

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"Substitute Specification"

PROCESS FOR FURTHER PROCESSING OF SMALL GLASS PARTICLES

BACKGROUND OF THE INVENTION

This invention relates to a process for the further processing of small glass particles, for example, in the form of scrap glass granulate with a grain size in the range between 0.3 and 4 mm, or glass beads with diameters in the range between 0.1 and 2.3 mm.

In our current industrial society very large amounts of scrap glass are formed. For environmental reasons, it therefore seems desirable for this scrap glass to be reused.

In this connection it is indeed possible for the scrap glass to be remelted in order to produce, for example, new bottles from it. The disadvantage of remelting scrap glass is due to homogenization and degassing of glass melts with temperatures in the range between 1400°C and 1600°C, which are necessary so that the remelting of scrap glass can only be accomplished with very high energy costs.

Within the framework of re-use of scrap glass, mainly small glass particles in the form of scrap glass granulate and spherical glass beads produced therefrom are available. The grain size of these glass particles can be very accurately set by screening.

The object of this invention is to provide a process with which further processing of these glass particles is possible at relatively low energy cost, using simple technical aids. New products formed can be used for very diverse purposes in industry.

SUMMARY OF THE INVENTION

Glass particles are produced with a relatively low energy cost. The surfaces of the glass particles are brought into contact with a low melting silicate flax or enamel, for example, lead borosilicate, sodium borosilicate, fluoro-borosilicate or mixtures thereof, in amounts of 2-9% by weight,

preferably 3-5% by weight. The glass particles are exposed to a heat treatment in the range of 540°C to 800°C, preferably in the range of 560°C to 660°C, at which the low melting silicate flax or enamel melts on the surfaces of the glass particles.

DETAILED DESCRIPTION OF THE INVENTION

Within the framework of the invention, the surfaces of existing glass particles are brought into contact with a low-melting silicate flux or enamel, whereupon at relatively low temperatures around 600°C and accordingly with low power consumption, a heat treatment is done, in which the low melting silicate flux or enamel is melted. Essentially this measure allows three different things.

1. A very economical color coating of the existing glass particles in the case of glass beads or glass granulates.
2. Very economical connection of one layer of glass particles on any carrier layer; in conjunction with flat glass, ceramic tiles, metal surfaces, glass films and/or ceramic fabrics this allows production of highly light reflective surfaces.
3. Very economical joining of glass particles among one another; this allows production of porous glass components, heat insulating glass, cladding panels and the like.

Other details of the invention follow from the following description.

1. Production of a color coating on glass beads or glass granulate

The raw materials used are uncolored glass beads or screened glass granulate, and particles of this type are made available by industry at very low prices. These glass beads have diameters in the range between 0.1 and 2.3 mm, or these glass granulates have a grain size between 0.3 and 4 mm, and are

subsequently wetted with a wetting agent in the form of an easily gasifying screen printing oil, a liquid which contains both boric acid and also fluorine salts, or mixtures thereof. While wetting takes place using the easily gasifying screen printing oil alone, the surface of the glass beads, or glass granulates, is softened by the liquid which contains both boric acid and also fluorine salts with the simultaneous action of heat, so that by suitably adjusting the ratio between the screen printing oil and the liquid which contains both boric acid and also fluorine salts, the thickness of the color coating, to be produced, can be adjusted at will.

Subsequently, the superficially treated glass particles are uniformly coated in a low melting enamel or flux, the color feed thereof, taking place in powder form. In this way a colored layer can be applied to the glass beads, or glass granulates, with the percentage by weight, generally in the range between 2 and 9%, by weight, preferably in the range between 3 and 5%, by weight.

The colored layer applied to the glass particles can now be fired on in two ways. In one case, the coated glass particles are caused to roll off over a slanted plane, consisting of stainless steel sheets, these stainless steel sheets being provided with a boron nitrite coating for protection. In doing so, the rolling glass particles traverse a thermal zone with temperatures in the range between 540°C and 800°C, preferably in the range between 560°C and 660°C; this causes the applied color layer to be fired onto and into the surface of the glass particles.

Alternatively, the glass particles, provided with a colored layer, can be placed in a mold which does not stick to them, for example, a ceramic fiber mold, or a mold consisting of refractory sheets, with a layer thickness of a maximum of 6 cm. The molds filled with the glass particles, are then placed in a furnace, whereupon the colored layer on the glass particles is fired on, and heated in the range between 540°C and 800°C, and

preferably in the range between 560°C and 660°C. In doing so however only spot connections of the glass particles placed in the respective molds among one another arise, which thus after cooling can be very easily pulverized within a corresponding mill, a pulverizing device, or using hard rubber, or hardwood rollers and can be isolated into colored glass particles separate from one another.

Since within the framework of the invention not all the glass particles in the form of glass beads, or glass granulates, are colored, but only a thin outside layer, glass particles colored in this way can be produced at a very low cost, because only relatively small amounts of expensive colored glass additives in the form of rare earths, and the like, are necessary. The described process allows easy, fast and extremely diverse coloring of glass particles, because the most varied color mixtures, as are supplied by companies such as Hereus and Degusa for the ceramic and glass refinement industry, can be used. Within the framework of mixing processes, any color shade can be established both for small and large amounts selectively for glass beads, or glass granulates.

The firing of metal oxide colors onto the surface of the glass particles, which is done within the framework of the invention, can be done selectively in an oxidizing or reducing atmosphere, yielding either transparent colors or metallic surfaces. The latter are important for desired heat or light reflection, and it should be mentioned that in a reducing atmosphere, special metal vapor deposition can be abandoned.

In the case of using copper oxide colors in an oxidizing atmosphere, blue and green colors result, while in a reducing atmosphere, yellow and red colors arise. When using bismuth oxide colors, on the other hand, in an oxidizing atmosphere, silvery colors arise. While using bismuth oxide in a reducing atmosphere, lemon yellow or gold colors are formed. Finally, when using silver oxide colors and salts, in the case of an oxidizing atmosphere, silvery surfaces can be achieved, and

while in a reducing atmosphere, yellow or lemon colors are formed.

Within the framework of the process, colored glass granulate provided with a colored outside layer can be used either as the raw material for Pate-de-Verre operations or a subsequent forming process can be carried out in which colored glass beads are produced from coated colored glass granulates. Forming of glass beads from originally colorless glass granulates, can be done selectively before or after application of an outer colored layer.

2. Application of one layer of glass beads or colored glass granulates on the surface of a carrier material.

In this case, the raw material can be any carrier material, for example, in the form of already fired or vitrified porcelain, stoneware, ceramic tiles, glass plates, glass films or bodies formed from these materials. These bodies can be vitrified brick, ceramic elements, tessellae, vessels, vases or any other bodies of this type.

Within the framework of the invention, a thin layer of a low melting silicate flux, or enamel, is applied to this carrier material either by means of a brush, a screen printing process, by spraying on, or by rolling on. Since these materials are generally powdered, they should be mixed with a liquid wetting agent, for example, in the form of an easily gasifying screen printing oil, so that in this way a viscous mass, which can be applied results. The low melting glass flux is chosen such that its melting point is below the temperature range between 540°C and 800°C, preferably below the temperature range between 560°C and 660°C. It can be for example a lead borosilicate, a sodium borosilicate, a fluoroborosilicate or special mixtures of these substances.

The carrier material coated with this low melting flux is subsequently provided with a single layer of small glass particles or glass granulates, the diameter of these glass

particles being in the range between 0.3 and 4 mm, or 0.1 and 2.3 mm. The application of these glass particles can be done either by immersion in a container filled with glass particles or within the framework of a sprinkling process carried out in the oblique position, in which excess glass particles roll off. The carrier material coated with a layer of glass particles is then placed in a corresponding furnace and heated to a temperature in the range between 540°C and 800°C, preferably in the range between 560°C and 660°C, the low melting flux being caused to melt. In doing so it can preferably be a tunnel kiln through which the coated carrier material is continually routed by a conveyor means.

After the cooling process, a very strong connection between the carrier material and the applied glass particles arises. The thickness of the applied flux layer should be chosen such that after the melting process, the applied glass particles are embedded in the layer of the low melting flux, in the range between one third and one half of the diameter.

To achieve special optical effects, the low melting glass flux, or the glass particles, can be selectively colored as desired. With respect to the application of differently colored glass particles, correspondingly formed templates can be used.

In the corresponding manner, metallic surfaces can be provided with a layer of colored or uncolored glass particles. In particular, small glass beads have the property that they act as strongly reflect light, so that in this way light-reflecting surfaces are produced. In doing so, for example, the body surfaces of motor vehicles are especially well suited, by which it is possible to better recognize these vehicles even under conditions of poor visibility, for example, in fog. The same of course applies to any other craft, such as ships and aircraft, with surfaces under certain circumstances which can be influenced by the grainy structure of the glass beads, such that reduced frictional resistance within fluid media results. For stationary

metallic surface, for example, the outside metallic facades of tall buildings, or in crash barriers on highways, it can be feasible, if they are provided with light-reflecting surfaces.

Within the framework of the invention, a ceramic fabric is also suitable as the carrier layer, in which the warp and weft threads are preferably looped. In this way, a very durable clothing, or tent fabric, is formed which as a result of its fire resistance and good reflection properties seems especially well suited especially for use in tropical and subtropical environments against strong external incident solar radiation. These light reflecting fabrics can also be used for hanging from ceilings, or as theater curtains.

3. Joining a large number of small glass particles among one another

Either glass beads or glass granulates can be used as the raw material for producing porous glass blocks. The glass granulates, are preferably granulates formed by the mechanical crushing of scrap glass, with the aid of screening glass particles with a grain size as uniform as possible being formed. In this case, glass granulates are used which have a uniform grain size between 0.3 and 4 mm. The glass beads can be spherical glass elements which have a diameter as uniform as possible, in the range between 0.1 and 2.3 mm.

The glass particles used to produce the respective glass blocks, are uniformly wetted within a suitable mixing device with an adhesive which gasifies without residue, for example, crystal ice cement 33 from Hereus. But likewise, an aqueous fluorine solidum boric acid solution, or a glaze binder of cellulose derivatives, or hydrophilic screen printing media which burn off without residue, can be used for this purpose.

Subsequently, 2 to 9% by weight, preferably 3 to 5% by weight, of a low melting silicate flux, or enamel in powder form, can be added, this flux consisting, for example, of lead borosilicate, sodium borosilicate, fluoroborosilicate or mixtures

thereof. Within a mixing device, this mixing process is continued until the glass particles are uniformly coated with this low melting silicate flux, or enamel.

The moldable mass produced in this way, is then formed into relief plates, glass blocks, wall panels, cladding panels, and the like, and is heated inside a corresponding furnace, preferably a tunnel kiln, to a temperature in the range between 540°C and 800°C, preferably in the range between 560°C and 660°C. Here the low melting silicate flux, or enamel, is caused to melt so that after cooling, between the individual glass particles there form bridges which impart the required mechanical strength to the respective glass component. The contact bridges, which have been formed, have sufficient elasticity so that even glass particles with different coefficients of thermal expansion can be joined to one another without flaws being formed within the glass component during temperature fluctuations, cooling processes, and the like. In spite of the different coefficients of thermal expansion of the glass particles used, glass blocks which are stress-free can be produced in this way. Since in these laminated materials, the mutual contact surfaces, between the glass particles, have diameters which must necessarily be less than 0.6 mm, in this way the thermal shock limit of the glass is not reached, so that temperature-caused breaks do not occur. Remaining residual stresses are conversely reduced via the existing heat conduction.

Since the individual glass particles are joined to one another only in the area of their points of mutual contact, a glass block is formed which has a relatively high porosity with low weight. When using glass beads as the raw material, glass blocks form with a specific weight of roughly 1.35, while when using glass granulate glass blocks are formed with a specific weight of roughly 1.25.

Compared to glass blocks of glass granulate, glass blocks of glass beads are distinguished by the fact that due to the exactly stipulated glass bead size both the pore size and

also the pore density can be very accurately set. In addition, the glass beads present within the respective glass blocks, especially in the surface area, cause strong light reflection of the incident light so that these glass blocks are especially well suited as decorative wall elements. In contrast, glass blocks produced from glass granulate exhibit a weakly sparkling effect which is caused by the different light reflection on the melted corners, edges and surfaces of the glass granulate used.

When using optically transparent glass particles and a likewise transparent low melting silicate flux, glass components are formed which at a thickness of roughly 5 cm have transparency of roughly 10%.

Colored glass blocks on the other hand can be produced by colored glass particles or correspondingly colored glass flux. In doing so, its seems plausible that coloring of the silicate flux or enamel represents the economical approach as a result of the much smaller amounts.

The glass components produced within the framework of this invention thus have the following advantages:

1. Compared to other glass laminate elements, they have a relatively low specific weight as a result of the existing pores.

2. Depending on the choice of glass particles used, the porosity of the glass block as claimed in the invention can be set differently so that in this way a certain breathability can be achieved.

3. To achieve different colorations, the most varied types of glass particles can be used without stress problems arising as a result of the different coefficients of thermal expansion.

4. Compared to solid glass elements the glass blocks as claimed in the invention are largely insensitive to thermal shock. The pertinent glass blocks have high thermal stability, according to which the surfaces of the glass blocks can be heated to above 800°C. Based on the air bubble inclusions overly fast

fusion of the glass particles together which are present within the glass blocks is prevented, even if fusion of the surfaces of the glass particles together takes place by the action of heat. If monoaluminum phosphate or ammonium or boron potassium compounds are additionally added to the glass block, nitrogen or expanding foams which prevent destruction by fire for hours develop within the glass block.

5. Furthermore, the glass blocks as claimed in the invention can also be statically loaded on a conditional basis, their being similar to conglomerate rock in their structure. The static loading capacity can be further increased by building up the connecting bridges using fluorosodium borosilicates. An increase of the static loading capacity however also arises by use of glass particle mixes of the same glass composition, or when using glass particles with highly varying grain size. For nonuniform loading, extensive load compensation is achieved via the existing contact bridges between the individual glass particles.

6. Glass blocks can be produced from the most varied scrap glass and require only additives in amounts between 2 and 9% by weight, preferably 3 and 5% by weight, so that these glass blocks can be produced very economically.

7. Compared to newly molten glass, the glass blocks in the invention can be produced with very low power consumption. The agglomeration time, for up to 60 mm thick plates, is roughly 30 minutes, while the cooling phase using capsule cooling without an energy supply, or by applying ceramic fiber mats, can be carried out within 90 minutes.

8. The resulting transparency of the glass blocks is reduced by the fusing together of glass particles with increasing wall thickness and color intensity. At temperatures of 750°C, the transparency can be increased again, the properties of the glass component being changed by the overall sintering of the mixture. In this way, a closed glass block with existing air inclusions and increased internal stresses is formed.

The glass components as embodied by the invention can be used as plates, relief panels, glass blocks, wall linings, cladding panels, decorative articles and many other applications. The glass components can be produced very economically, production costs amounting to roughly 650.00 DM per ton when using scrap glass granulate.

If the pasty mass consisting of glass particles, low-melting flux and liquid wetting agents, before the burning process, is placed in the intermediate space between two flat glass plates and then heat treatment is done, very effective heat-insulating panes can be produced in this way.

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"marked up Specification"

Christian Klepsch, A-5201 Seekirchen and

Sarolf Sauer, A-1130 Vienna

Process for further processing of small glass particles

BACKGROUND OF THE INVENTION

This invention relates to a process for the further processing of small glass particles, for example, in the form of scrap glass granulate with a grain size in the range between 0.3 and 4 mm, or glass beads with diameters in the range between ~~01~~ 0.1. and 2.3 mm.

In our current industrial society very large amounts of scrap glass are formed. For environmental reasons, it therefore seems desirable for this scrap glass to be reused.

In this connection it is indeed possible for the scrap glass to be remelted in order to produce, for example, new bottles from it. The disadvantage of remelting scrap glass is due to ~~But here the disadvantage is the circumstance that for~~ homogenization and degassing of glass melts with temperatures in the range between 1400°C and 1600°C, which are necessary so that the remelting of scrap glass can only be ~~done~~ accomplished with very high energy costs.

Within the framework of re-use of scrap glass, mainly small glass particles in the form of scrap glass granulate and spherical glass beads produced therefrom are available. The grain size of these glass particles can ~~thus~~ be very accurately set by screening.

The object of this invention is to ~~devise~~ provide a process with which further processing of these glass particles is possible ~~with~~ at relatively low energy cost, using simple technical aids. New products ~~being~~ formed ~~which~~ can be used for very diverse purposes in industry.

~~As claimed in the invention this is done by using~~ the process steps cited in the characterizing ~~part of claim 1.~~

Ad~~vantageous embodiments~~ of the inven~~tion arise on the basis~~ of ~~dependent claims 2 to 11.~~

DETAILED DESCRIPTION OF THE INVENTION

Within the framework of the invention, the surfaces of existing glass particles are brought into contact with a low-melting silicate flux or enamel, whereupon at relatively low temperatures around 600°C and accordingly with low power consumption, a heat treatment is done, in which the low melting silicate flux or enamel is melted. Essentially this measure allows three different things.

1. A very economical color coating of the existing glass particles in the case of glass beads or glass granulates.
2. Very economical connection of one layer of glass particles on any carrier layer; in conjunction with flat glass, ceramic tiles, metal surfaces, glass films and/or ceramic fabrics this allows production of highly light reflective surfaces.

SUMMARY OF THE INVENTION

Glass particles are produced with a relatively low energy cost. The surfaces of the glass particles are brought into contact with a low melting silicate flux or enamel, for example, lead borosilicate, or sodium borosilicate, fluoroborosilicate or mixtures thereof, in amounts [illegible]

3. Very economical joining of glass particles among one another; this allows production of porous glass components, heat insulating glass, cladding panels and the like.

Other details of the invention follow from the following description.

1. <u>Production of a color coating on glass beads or glass granulate</u>

The raw materials used are uncolored glass beads or screened glass granulate, and particles of this type are made available by industry at very low prices. These glass beads ~~with~~ have diameters in the range between 0.1 and 2.3 mm, or these glass granulates ~~with~~ have a grain size between 0.3 and 4 mm, and are subsequently wetted with a wetting agent in the form of an easily gasifying screen printing oil, a liquid which contains both boric acid and also fluorine salts, or mixtures thereof. While wetting takes place using the easily gasifying screen printing oil alone, ~~surface~~, the surface of the glass beads, or glass granulates, is softened by the liquid which contains both boric acid and also fluorine salts with the simultaneous action of heat, so that by suitably adjusting the ratio between the screen printing oil and the liquid which contains both boric acid and also fluorine salts, the thickness of the color coating, to be produced, can be adjusted at will.

Subsequently, the superficially treated glass particles are uniformly coated in a low melting enamel or flux, the color, feed thereof, taking place in powder form. In this way a colored layer

can be applied to the glass beads, or glass granulates, with ~~a~~ the percentage by weight, generally in the range between 2 and 9%, by weight, preferably in the range between 3 and 5%, by weight.

The colored layer applied to the glass particles can now be fired on in two ways. In one case, the coated glass particles are caused to roll off over a slanted plane, consisting of stainless steel sheets, these stainless steel sheets being provided with a boron nitrite coating for protection. In doing so, the rolling glass particles traverse a thermal zone with temperatures in the range between 540°C and 800°C, preferably in the range between 560°C and 660°C; this causes the applied color layer to be fired onto and into the surface of the glass particles.

Alternatively, the glass particles, provided with a colored layer, can ~~likewise~~ be placed in a mold which does not stick to them, for example, a ceramic fiber mold, or a mold consisting of refractory sheets, with a layer thickness of a maximum of 6 cm. The molds filled with the glass particles, are then placed in a furnace, whereupon the colored layer on the glass particles is fired on, ~~when~~ and heated in the range between 540°C and 800°C, and preferably in the range between 560°C and 660°C. In doing so however only spot connections of the glass particles placed in the respective molds among one another arise, which thus after cooling can be very easily pulverized within a corresponding mill, a pulverizing device, or using hard rubber, or hardwood

rollers and can be isolated into colored glass particles separate from one another.

Since within the framework of the invention not all the glass particles in the form of glass beads, or glass granulates, are colored, but only a thin outside layer, glass particles colored in this way can be produced at a very low cost, because only relatively small amounts of expensive colored glass additives in the form of rare earths, and the like, are necessary. The described process ~~thus~~ allows easy, fast and extremely diverse coloring of ~~the~~ glass particles, because the most varied color mixtures, as are supplied by companies such as Hereus and Degusa for the ceramic and glass refinement industry, can be used. Within the framework of mixing processes, ~~thus~~ any color shade~~s~~ can be established both for small and ~~also~~ large amounts selectively for glass beads, or ~~also~~ glass granulates.

The firing of metal oxide colors onto the surface of the glass particles, which is done within the framework of the invention, can be done selectively in an oxidizing or reducing atmosphere, yielding either transparent colors or metallic surfaces. The latter are important for desired heat or light reflection, and it should be mentioned that in a reducing atmosphere, special metal vapor deposition can be abandoned.

In the case of using copper oxide colors in an oxidizing atmosphere, blue and green colors result, while in a reducing atmosphere, yellow and red colors arise. When using bismuth oxide

colors, on the other hand, in an oxidizing atmosphere, silvery colors arise. While using bismuth oxide in a reducing atmosphere, lemon yellow or gold colors are formed. Finally, when using silver oxide, colors and salts, in the case of an oxidizing atmosphere, silvery surfaces can be achieved, and while in a reducing atmosphere, yellow or lemon colors are formed.

Within the framework of the process ~~as claimed in the invention~~, colored glass granulate provided with a colored outside layer can be used either as the raw material for Pate-de-Verre operations or a subsequent forming process can be carried out in which colored glass beads are produced from coated colored glass granulates. Forming of glass beads from originally colorless glass granulates, can ~~thus~~ be done selectively before or after application of an outer colored layer.

2. <u>Application of one layer of glass beads or colored glass granulates on the surface of a carrier material.</u>

In this case, the raw material can be any carrier material, for example, in the form of already fired or vitrified porcelain, stoneware, ~~or~~ ceramic tiles, glass plates, ~~or~~ glass films or bodies formed from these materials. These bodies can be ~~for example~~ vitrified brick, ceramic elements, tessellae, vessels, ~~or~~ vases or any other bodies of this type.

Within the framework of the invention, a thin layer of a low melting silicate flux, or enamel, is applied to this carrier

material either by means of a brush, a screen printing process, by spraying on, or by rolling on. Since these materials are generally powdered, they should be mixed with a liquid wetting agent, for example, in the form of an easily gasifying screen printing oil, so that in this way a viscous mass, which can be applied results. The low melting glass flux is chosen such that its melting point is below the temperature range between 540°C and 800°C, preferably below the temperature range between 560°C and 660°C. It can be for example a lead borosilicate, a sodium borosilicate, a fluoroborosilicate or special mixtures of these substances.

The carrier material coated with this low melting flux is subsequently provided with a single layer of small glass particles or glass granulates, the diameter of these glass particles being in the range between 0.3 and 4 mm, or 0.1 and 2.3 mm. The application of these glass particles can be done either by immersion in a container filled with glass particles or within the framework of a sprinkling process carried out in the oblique position, in which excess glass particles roll off. The carrier material coated with a layer of glass particles is then placed in a corresponding furnace and heated to a temperature in the range between 540°C and 800°C, preferably in the range between 560°C and 660°C, the low melting flux being caused to melt. In doing so it can preferably be a tunnel kiln through which the coated carrier material is continually routed by a conveyor means.

After the cooling process, ~~in this way~~ a very strong connection between the carrier material and the applied glass particles arises. The thickness of the applied flux layer should be chosen such that after the melting process, the applied glass particles are embedded in the layer of the low melting flux, in the range between one third and one half of the diameter.

To achieve special optical effects, the low melting glass flux, or the glass particles, can be selectively colored as desired. With respect to the application of ~~the~~ differently colored glass particles, ~~furthermore the~~ correspondingly formed templates can be used.

In the corresponding manner, ~~also~~ metallic surfaces can be provided with a layer of colored or uncolored glass particles. In particular, small glass beads have the property that they act as strongly light~~-~~reflect~~ing~~, so that in this way light-reflecting surfaces are produced. In doing so, for example, the body surfaces of motor vehicles are especially well suited, by which it is possible to better recognize these vehicles even under conditions of poor visibility, for example, in fog. The same of course applies to any other craft, such as ships and aircraft, with surfaces under certain circumstances which can be influenced by the grainy structure of the glass beads, such that reduced frictional resistance within fluid media results. ~~Also~~ For metallic surfaces ~~located~~ stationary, for example, the outside metallic ~~outside~~ facades of tall buildings, or in ~~the~~ crash barriers on

highways, it can ~~also~~ be feasible, if they are provided with light-reflecting surfaces.

Within the framework of the invention, a ceramic fabric is also suitable as the carrier layer, in which the warp and weft threads are preferably looped. In this way, a very durable clothing, or tent fabric, is formed which as a result of its fire resistance and good reflection properties seems especially well suited especially for use in tropical and subtropical environments against strong external incident solar radiation. These light reflecting fabrics can also be used for hanging from ceilings, or as theater curtains.

3. Joining a large number of small glass particles among one another

Either glass beads or glass granulates can be used as the raw material for producing porous glass blocks. The glass granulates, are preferably granulates~~, as are~~ formed by the mechanical crushing of scrap glass, with the aid of screening glass particles with a grain size as uniform as possible being formed. In this case, glass granulates are used which have a uniform grain size between 0.3 and 4 mm. The glass beads can ~~on the other hand~~ be spherical glass elements which have a diameter as uniform as possible, in the range between 0.1 and 2.3 mm.

The glass particles ~~to be~~ used to produce the respective glass blocks, are uniformly wetted within a suitable mixing device

with an adhesive which gasifies without residue, for example, crystal ice cement 33 from Hereus. But likewise, an aqueous fluorine solidum boric acid solution, or a glaze binder of cellulose derivatives, or hydrophilic screen printing media which burn off without residue, can be used for this purpose.

Subsequently, 2 to 9% by weight, preferably 3 to 5% by weight, of a low melting silicate flux, or enamel in powder form, can be added, this flux consisting, for example, of lead borosilicate, sodium borosilicate, fluoroborosilicate or mixtures thereof. Within a mixing device, this mixing process is continued until the glass particles are uniformly coated with this low melting silicate flux, or enamel.

The moldable mass produced in this way, is then formed into relief plates, glass blocks, wall panels, cladding panels, and the like, and is heated inside a corresponding furnace, preferably a tunnel kiln, to a temperature in the range between 540°C and 800°C, preferably in the range between 560°C and 660°C. Here the low melting silicate flux, or enamel, is caused to melt so that after cooling, between the individual glass particles there form bridges which impart the required mechanical strength to the respective glass component. The contact bridges, which have been formed, have sufficient elasticity so that even glass particles with different coefficients of thermal expansion can be joined to one another without flaws being formed within the glass component during temperature fluctuations, cooling processes, and the like.

In spite of the different coefficients of thermal expansion of the glass particles used, glass blocks which are ~~essentially~~ stress-free can be produced in this way. Since in these laminated materials, the mutual contact surfaces, between the glass particles, have diameters which must necessarily be less than 0.6 mm, in this way the thermal shock limit of the glass is not reached, so that temperature-caused breaks do not occur. Remaining residual stresses are conversely reduced via the existing heat conduction.

Since the individual glass particles are joined to one another only in the area of their points of mutual contact, ~~in this way~~ a glass block is formed which has a relatively high porosity with low weight. When using glass beads as the raw material, t~~herefor~~e glass blocks form with a specific weight of roughly 1.35, while when using glass granulate glass blocks are formed with a specific weight of roughly 1.25.

Compared to glass blocks of glass granulate, glass blocks of glass beads are distinguished by the fact that due to the exactly stipulated glass bead size both the pore size and also the pore density can be very accurately set. In addition, the glass beads present within the respective glass blocks, especially in the surface area, cause strong light reflection of the incident light so that these glass blocks are especially well suited as decorative wall elements. In contrast, ~~the~~ glass blocks produced from glass granulate exhibit a weakly sparkling effect which is

caused by the different light reflection on the melted corners, edges and surfaces of the glass granulate used.

When using optically transparent glass particles and a likewise transparent low melting silicate flux, glass components are formed which at a thickness of roughly 5 cm have transparency of roughly 10%.

Colored glass blocks on the other hand can be produced by colored glass particles or correspondingly colored glass flux. In doing so, its seems plausible that coloring of the silicate flux or enamel represents the economical approach as a result of the much smaller amounts.

The glass components produced within the framework of this invention thus have the following advantages:

1. Compared to other glass laminate elements, they have a relatively low specific weight as a result of the existing pores.

2. Depending on the choice of glass particles used, the porosity of the glass block as claimed in the invention can be set differently so that in this way a certain breathability can be achieved.

3. To achieve different colorations, the most varied types of glass particles can be used without stress problems arising as a result of the different coefficients of thermal expansion.

4. Compared to solid glass elements the glass blocks as claimed in the invention are largely insensitive to thermal shock. The pertinent glass blocks have high thermal stability,

according to which the surfaces of the glass blocks can be heated to above 800°C. Based on the air bubble inclusions overly fast fusion of the glass particles together which are present within the glass blocks is prevented, even if fusion of the surfaces of the glass particles together takes place by the action of heat. If monoaluminum phosphate or ammonium or boron potassium compounds are additionally added to the glass block, nitrogen or expanding foams which prevent destruction by fire for hours develop within the glass block.

5. Furthermore, the glass blocks as claimed in the invention can also be statically loaded on a conditional basis, their being similar to conglomerate rock in their structure. The static loading capacity can be further increased by building up the connecting bridges using fluorosodium borosilicates. An increase of the static loading capacity however also arises by use of glass particle mixes of the same glass composition, or when using glass particles with highly varying grain size. For nonuniform loading, extensive load compensation is achieved via the existing contact bridges between the individual glass particles.

6. ~~The~~ Glass blocks ~~as claimed in the invention~~ can be produced from the most varied scrap glass and require only additives in amounts between 2 and 9% by weight, preferably 3 and 5% by weight, so that these glass blocks can be produced very economically.

7. Compared to newly molten glass, the glass blocks ~~as claimed~~ in the invention can ~~furthermore~~ be produced with very low power consumption. The agglomeration time, for ~~of~~ up to 60 mm thick plates, is ~~only~~ roughly 30 minutes, while the cooling phase using capsule cooling, without an energy supply, or by applying ceramic fiber mats, can be carried out within 90 minutes.

8. The resulting transparency of the glass blocks ~~as claimed in the invention~~ is reduced by the fusing together of glass particles with increasing wall thickness and color intensity. At temperatures of 750°C, the transparency ~~however~~ can be increased again, the properties of the glass component ~~then~~ being changed by the overall sintering of the mixture. In this way, ~~then~~ a closed glass block with existing air inclusions and increased internal stresses is formed.

The glass components as embodied by ~~claimed in~~ the invention can be used as plates, relief panels, glass blocks, wall linings, cladding panels, decorative articles and many other applications. The glass components can ~~thus~~ be produced very economically, production costs amounting to roughly 650.00 DM per ton when using scrap glass granulate.

If the pasty mass consisting of glass particles, low-melting flux and liquid wetting agents, before the burning process, is placed in the intermediate space between two flat glass plates and then heat treatment is done, very effective heat-insulating panes can be produced in this way.

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Process for further processing of small glass particles

This invention relates to a process for further processing of small glass particles, for example in the form of scrap glass granulate with a grain size in the range between 0.3 and 4 mm or glass beads with diameters in the range between 01. and 2.3 mm.

In our current industrial society very large amounts of scrap glass are formed. For environmental reasons it therefore seems desirable for this scrap glass to be reused.

In this connection it is indeed possible for the scrap glass to be remelted in order to produce for example new bottles from it. But here the disadvantage is the circumstance that for homogenization and degassing of glass melts temperatures in the range between 1400 and 1600°C are necessary so that the remelting of scrap glass can only be done with very high energy cost.

Within the framework of re-use of scrap glass, mainly small glass particles in the form of scrap glass granulate and spherical glass beads produced therefrom are available. The grain size of these glass particles can thus be very accurately set by screening.

The object of this invention is to devise a process with which further processing of these glass particles is possible with relatively low energy cost, using simple technical aids, new

products being formed which can be used for very diverse purposes in industry.

As claimed in the invention this is done by using the process steps cited in the characterizing part of claim 1.

Advantageous embodiments of the invention arise on the basis of dependent claims 2 to 11.

Within the framework of the invention the surfaces of existing glass particles are brought into contact with a low-melting silicate flux or enamel, whereupon at relatively low temperatures around 600°C and accordingly with low power consumption heat treatment is done, in which the low melting silicate flux or enamel is melted. Essentially this measure allows three different things.

1. A very economical color coating of the existing glass particles in the case of glass beads or glass granulates.
2. Very economical connection of one layer of glass particles on any carrier layer; in conjunction with flat glass, ceramic tiles, metal surfaces, glass films and/or ceramic fabrics this allows production of highly light reflective surfaces.
3. Very economical joining of glass particles among one another; this allows production of porous glass components, heat insulating glass, cladding panels and the like.

Other details of the invention follow from the following description.

1. <u>Production of a color coating on glass beads or glass granulate</u>

The raw materials used are uncolored glass beads or screened glass granulate, and particles of this type are made available by industry at very low prices. These glass beads with diameters in the range between 0.1 and 2.3 mm or glass granulates with a grain size between 0.3 and 4 mm are subsequently wetted with a wetting agent in the form of an easily gasifying screen printing oil, a liquid which contains both boric acid and also fluorine salts or mixtures thereof. While wetting takes place using the easily gasifying screen printing oil alone surface, the surface of the glass beads or glass granulates is softened by the liquid which contains both boric acid and also fluorine salts with the simultaneous action of heat, so that by suitably adjusting the ratio between the screen printing oil and the liquid which contains both boric acid and also fluorine salts the thickness of the color coating to be produced can be adjusted at will.

Subsequently, the superficially treated glass particles are uniformly coated in a low melting enamel or flux color, feed thereof taking place in powder form. In this way a colored layer can be applied to the glass beads or glass granulates with a percentage by weight generally in the range between 2 and 9% by weight, preferably in the range between 3 and 5% by weight.

The colored layer applied to the glass particles can now be fired on in two ways. In one case the coated glass particles are caused to roll off over a slanted plane consisting of stainless steel sheets, these stainless steel sheets being provided with a boron nitrite coating for protection. In doing so the rolling glass particles traverse a thermal zone with temperatures in the

range between 540 and 800°C, preferably in the range between 560 and 660°C; this causes the applied color layer to be fired onto and into the surface of the glass particles.

Alternatively, the glass particles provided with a colored layer can likewise be placed in a mold which does not stick to them, for example a ceramic fiber mold or a mold consisting of refractory sheets, with a layer thickness of a maximum 6 cm. The molds filled with the glass particles are then placed in a furnace, whereupon the colored layer on the glass particles is fired on when heated in the range between 540 and 800°C, preferably in the range between 560 and 660°C. In doing so however only spot connections of the glass particles placed in the respective molds among one another arise, which thus after cooling can be very easily pulverized within a corresponding mill, a pulverizing device or using hard rubber or hardwood rollers and can be isolated into colored glass particles separate from one another.

Since within the framework of the invention not all the glass particles in the form of glass beads or glass granulates are colored, but only a thin outside layer, glass particles colored in this way can be produced at very low cost because only relatively small amounts of expensive colored glass additives in the form of rare earths and the like are necessary. The described process thus allows easy, fast and extremely diverse coloring of the glass particles, because the most varied color mixtures, as are supplied by companies such as Hereus and Degusa for the ceramic and glass refinement industry, can be used.

Within the framework of mixing processes thus any color shades can be established both for small and also large amounts selectively for glass beads or also glass granulates.

The firing of metal oxide colors onto the surface of the glass particles which is done within the framework of the invention can be done selectively in an oxidizing or reducing atmosphere, yielding either transparent colors or metallic surfaces. The latter are important for desired heat or light reflection, and it should be mentioned that in a reducing atmosphere special metal vapor deposition can be abandoned.

In the case of using copper oxide colors in an oxidizing atmosphere blue and green colors result, while in a reducing atmosphere yellow and red colors arise. When using bismuth oxide colors on the other hand in an oxidizing atmosphere silvery colors arise, while in a reducing atmosphere lemon yellow or gold colors are formed. Finally, when using silver oxide colors and salts in the case of an oxidizing atmosphere silvery surfaces can be achieved, while in a reducing atmosphere yellow or lemon colors are formed.

Within the framework of the process as claimed in the invention, colored glass granulate provided with a colored outside layer can be used either as the raw material for Pate-de-Verre operations or a subsequent forming process can be carried out in which colored glass beads are produced from coated colored glass granulates. Forming of glass beads from originally colorless glass granulates can thus be done selectively before or after application of an outer colored layer.

2. Application of one layer of glass beads or colored glass granulates on the surface of a carrier material.

In this case the raw material can be any carrier material for example in the form of already fired or vitrified porcelain, stoneware or ceramic tiles, glass plates or glass films or bodies formed from these materials. These bodies can be for example vitrified brick, ceramic elements, tessellae, vessels or vases or any other bodies of this type.

Within the framework of the invention a thin layer of a low melting silicate flux or enamel is applied to this carrier material either by means of a brush, a screen printing process, by spraying on or by rolling on. Since these materials are generally powdered, they should be mixed with a liquid wetting agent, for example in the form of an easily gasifying screen printing oil so that in this way a viscous mass which can be applied results. The low melting glass flux is chosen such that its melting point is below the temperature range between 540 and 800°C, preferably below the temperature range between 560 and 660°C. It can be for example a lead borosilicate, a sodium borosilicate, a fluoroborosilicate or special mixtures of these substances.

The carrier material coated with this low melting flux is subsequently provided with a single layer of small glass particles or glass granulates, the diameter of these glass particles being in the range between 0.3 and 4 mm or 0.1 and 2.3 mm. The application of these glass particles can be done either by immersion in a container filled with glass particles or within

the framework of a sprinkling process carried out in the oblique position, in which excess glass particles roll off. The carrier material coated with a layer of glass particles is then placed in a corresponding furnace and heated to a temperature in the range between 540 and 800°C, preferably in the range between 560 and 660°C, the low melting flux being caused to melt. In doing so it can preferably be a tunnel kiln through which the coated carrier material is continually routed by a conveyor means.

After the cooling process, in this way a very strong connection between the carrier material and the applied glass particles arises. The thickness of the applied flux layer should be chosen such that after the melting process the applied glass particles are embedded in the layer of the low melting flux in the range between one third and one half of the diameter.

To achieve special optical effects, the low melting glass flux or the glass particles can be selectively colored as desired. With respect to the application of the differently colored glass particles, furthermore the correspondingly formed templates can be used.

In the corresponding manner also metallic surfaces can be provided with a layer of colored or uncolored glass particles. In particular small glass beads have the property that they act as strongly light-reflecting so that in this way light-reflecting surfaces are produced. In doing so for example the body surfaces of motor vehicles are especially well suited, by which it is possible to better recognize these vehicles even under conditions of poor visibility, for example, in fog. The same of course

applies to any other craft, such as ships and aircraft with surfaces under certain circumstances which can be influenced by the grainy structure of the glass beads such that reduced frictional resistance within fluid media results. Also for metallic surfaces located stationary, for example the metallic outside facades of tall buildings or in the crash barriers on highways, it can also be feasible if they are provided with light-reflecting surfaces.

Within the framework of the invention a ceramic fabric is also suitable as the carrier layer, in which the warp and weft threads are preferably looped. In this way a very durable clothing or tent fabric is formed which as a result of its fire resistance and good reflection properties seems especially well suited especially for use in tropical and subtropical environments against strong external incident solar radiation. These light reflecting fabrics can also be used for hanging from ceilings or as theater curtains.

3. Joining a large number of small glass particles among one another

Either glass beads or glass granulates can be used as the raw material for producing porous glass blocks. The glass granulates are preferably granulates as are formed by mechanical crushing of scrap glass, with the aid of screening glass particles with a grain size as uniform as possible being formed. In this case glass granulates are used which have a uniform grain size between 0.3 and 4 mm. The glass beads can on the other hand

be spherical glass elements which have a diameter as uniform as possible in the range between 0.1 and 2.3 mm.

The glass particles to be used to produce the respective glass blocks are uniformly wetted within a suitable mixing device with an adhesive which gasifies without residue, for example crystal ice cement 33 from Hereus. But likewise an aqueous fluorine solidum boric acid solution or a glaze binder of cellulose derivatives or hydrophilic screen printing media which burn off without residue can be used for this purpose.

Subsequently, 2 to 9% by weight, preferably 3 to 5% by weight of a low melting silicate flux or enamel in powder form, can be added, this flux consisting for example of lead borosilicate, sodium borosilicate, fluoroborosilicate or mixtures thereof. Within a mixing device this mixing process is continued until the glass particles are uniformly coated with this low melting silicate flux or enamel.

The moldable mass produced in this way is then formed into relief plates, glass blocks, wall panels, cladding panels and the like and is heated inside a corresponding furnace, preferably a tunnel kiln, to a temperature in the range between 540 and 800°C, preferably in the range between 560 and 660°C. Here the low melting silicate flux or enamel is caused to melt so that after cooling, between the individual glass particles there form bridges which impart the required mechanical strength to the respective glass component. The contact bridges which have been formed have sufficient elasticity so that even glass particles with different coefficients of thermal expansion can be joined to

one another without flaws being formed within the glass component during temperature fluctuations, cooling processes and the like. In spite of the different coefficients of thermal expansion of the glass particles used, glass blocks which are essentially stress-free can be produced in this way. Since in these laminated materials the mutual contact surfaces between the glass particles have diameters which must necessarily be less than 0.6 mm, in this way the thermal shock limit of the glass is not reached, so that temperature-caused breaks do not occur. Remaining residual stresses are conversely reduced via the existing heat conduction.

Since the individual glass particles are joined to one another only in the area of their points of mutual contact, in this way a glass block is formed which has a relatively high porosity with low weight. When using glass beads as the raw material therefore glass blocks form with a specific weight of roughly 1.35, while when using glass granulate glass blocks are formed with a specific weight of roughly 1.25.

Compared to glass blocks of glass granulate, glass blocks of glass beads are distinguished by the fact that due to the exactly stipulated glass bead size both the pore size and also the pore density can be very accurately set. In addition, the glass beads present within the respective glass blocks, especially in the surface area, cause strong light reflection of the incident light so that these glass blocks are especially well suited as decorative wall elements. In contrast, the glass blocks produced from glass granulate exhibit a weakly sparkling effect which is

caused by the different light reflection on the melted corners, edges and surfaces of the glass granulate used.

When using optically transparent glass particles and a likewise transparent low melting silicate flux, glass components are formed which at a thickness of roughly 5 cm have transparency of roughly 10%.

Colored glass blocks on the other hand can be produced by colored glass particles or correspondingly colored glass flux. In doing so its seems plausible that coloring of the silicate flux or enamel represents the economical approach as a result of the much smaller amounts.

The glass components produced within the framework of this invention thus have the following advantages:

1. Compared to other glass laminate elements, they have a relatively low specific weight as a result of the existing pores.

2. Depending on the choice of glass particles used the porosity of the glass block as claimed in the invention can be set differently so that in this way a certain breathability can be achieved.

3. To achieve different colorations, the most varied types of glass particles can be used without stress problems arising as a result of the different coefficients of thermal expansion.

4. Compared to solid glass elements the glass blocks as claimed in the invention are largely insensitive to thermal shock. The pertinent glass blocks have high thermal stability, according to which the surfaces of the glass blocks can be heated to above 800°C. Based on the air bubble inclusions overly fast

fusion of the glass particles together which are present within the glass blocks is prevented even if fusion of the surfaces of the glass particles together takes place by the action of heat. If monoaluminum phosphate or ammonium or boron potassium compounds are additionally added to the glass block, nitrogen or expanding foams which prevent destruction by fire for hours develop within the glass block.

5. Furthermore, the glass blocks as claimed in the invention can also be statically loaded on a conditional basis, their being similar to conglomerate rock in their structure. The static loading capacity can be further increased by building up the connecting bridges using fluorosodium borosilicates. An increase of the static loading capacity however also arises by use of glass particle mixes of the same glass composition or when using glass particles with highly varying grain size. For nonuniform loading, extensive load compensation is achieved via the existing contact bridges between the individual glass particles.

6. The glass blocks as claimed in the invention can be produced from the most varied scrap glass and require only additives in amounts between 2 and 9% by weight, preferably 3 and 5% by weight, so that these glass blocks can be produced very economically.

7. Compared to newly molten glass the glass blocks as claimed in the invention can furthermore be produced with very low power consumption. The agglomeration time of up to 60 mm thick plates is only roughly 30 minutes, while the cooling phase

using capsule cooling without energy supply or by applying ceramic fiber mats can be carried out within 90 minutes.

8. The resulting transparency of the glass blocks as claimed in the invention is reduced by the fusing together of glass particles with increasing wall thickness and color intensity. At temperatures of 750°C the transparency however can be increased again, the properties of the glass component then being changed by overall sintering of the mixture. In this way then a closed glass block with existing air inclusions and increased internal stresses is formed.

The glass components as claimed in the invention can be used as plates, relief panels, glass blocks, wall linings, cladding panels, decorative articles and many other applications. The glass components can thus be produced very economically, production costs amounting to roughly 650.00 DM per ton when using scrap glass granulate.

If the pasty mass consisting of glass particles, low-melting flux and liquid wetting agents before the burning process is placed in the intermediate space between two flat glass plates and then heat treatment is done, very effective heat-insulating panes can be produced in this way.

#3

PTO/PCT Rec'd 03 APR 2000

Claims

1. Process for further processing of small glass particles, for example in the form of scrap glass granulate with a grain size in the range between 0.3 and 4 mm or glass beads with diameters in the range between 01. and 2.3 mm, characterized in that the surfaces of the glass particles are brought into contact with a low melting silicate flux or enamel, for example of lead borosilicate, sodium borosilicate, fluoroborosilicate or mixtures thereof in amounts of 2 to 9% by weight, preferably 3 to 5% by weight, and that as a result the glass particles are exposed to heat treatment in the range between 540 and 800°C, preferably in the range between 560 and 660°C, at which the low melting silicate flux or enamel melts on the surfaces of the glass particles.

2. Process as claimed in claim 1, wherein the surfaces of the glass particles, before making contact with the silicate flux or enamel, are treated beforehand with a wetting agent in the form of an screen printing oil which gasifies without residue, a liquid which contains both boric acid and also fluorine salts and/or mixtures thereof.

3. Process as claimed in claim 1 or 2, wherein the low melting silicate flux or enamel contains color pigments so that subsequent to heat treatment and a possibly necessary separation process, pulverizing or grinding forms small glass particles in the form of glass granulate or glass beads with a color layer fired onto the outside.

4. Process as claimed in claim 3, wherein heat treatment is done selectively in an oxidizing or reducing atmosphere.

5. Process as claimed in one of claims 1 to 4, wherein a layer of a low melting silicate flux or enamel is applied to one or both surfaces of a flat material, wherein consequently a layer of selectively colored or uncolored glass particles is applied to one or both wetted surfaces of the flat carrier material within the framework of a spraying process, and wherein following a completed rolling process heat treatment is done in which the formation of securely adhering connecting bridges between the glass particles among one another and the surface of the flat carrier material occurs.

6. Process as claimed in claim 5, wherein the flat carrier material is selectively thin flat glass or a flexible glass film.

7. Process as claimed in claim 5, wherein the flat carrier material is made in the form of ceramic tiles.

8. Process as claimed in claim 5, wherein the flat carrier material is formed by the extensive metal surfaces of the bodies of land vehicles or the surfaces of ship hulls or aircraft.

9. Process as claimed in claim 5, wherein the flat carrier material is a fireproof fabric preferably in the form of a looped glass fabric or ceramic fabric.

10. Process as claimed in one of claims 1 to 4, wherein the colored or uncolored glass beads are coated with a low melting silicate flux or enamel within a mixing device, whereupon the pasty mass produced in this way is placed in corresponding molds, by which after heat treatment porous glass elements are formed in

the form of flat plates, relief panels, glass blocks, wall panels, cladding panels and the like.

11. Process as claimed in one of claims 1 to 4, wherein the glass particles are coated with a low melting silicate flux or enamel within a mixing device, whereupon the pasty mass produced in this way is placed in a cavity between two flat glass plates or glass films, by which after heat treatment heat insulating glass panes are formed.

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Declaration and Power of Attorney for Patent Application
Erklärung für Patentanmeldungen mit Vollmacht

German Language Declaration

Als nachstehend benannter Erfinder erkläre ich hiermit an Eides Statt:

As a below named inventor, I hereby declare that:

daß mein Wohnsitz, meine Postanschrift und meine Staatsangehorigkeit den im nachstehenden nach meinem Namen aufgeführten Angaben entsprechen, daß ich nach bestem Wissen der ursprüngliche, erste und alleinige Erfinder (falls nachstehend nur ein Name angegeben ist) oder ein ursprünglicher, erster und Miterfinder (falls nachstehend mehrere Namen aufgeführt sind) des Gegenstandes bin, für den dieser Antrag gestellt wird und für den ein Patent für die Erfindung mit folgendem Titel beantragt wird:

My residence, post office address and citizenship are as stated next to my name

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PROCESS FOR FURTHER PROCESSING OF SMALL GLASS PARTICLES

deren Beschreibung hier beigefügt ist, es sei denn (in diesem Falle Zutreffendes bitte ankreuzen), diese Erfindung

☐ wurde angemeldet am ______________ unter der US-Anmeldenummer oder unter der Internationalen Anmeldenummer im Rahmen des Vertrags über die Zusammenarbeit auf dem Gebiet des Patentwesens (PCT) ______________ und am ______________ abgeändert (falls zutreffend).

the specification of which is attached hereto unless the following box is checked.

☒ was filed on 28 December 1999 as United States Application Number or PCT International Application Number 09/446,128 and was amended on ______________ (if applicable).

Ich bestätige hiermit, daß ich den Inhalt der oben angegebenen Patentanmeldung, einschließlich der Ansprüche, die eventuell durch einen oben erwähnten Zusatzantrag abgeändert wurde, durchgesehen und verstanden habe.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

Ich erkenne meine Pflicht zur Offenbarung jeglicher Informationen an, die zur Prüfung der Patentfähigkeit in Einklang mit Titel 37, Code of Federal Regulations, § 1.56 von Belang sind.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

Burden Hour Statement: This form is estimated to take 0.4 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231.

German Language Declaration

Ich beanspruche hiermit ausländische Prioritätsvorteile gemäß Title 35, US-Code, § 119 (a)-(d), bzw. § 365(b) aller unten aufgeführten Auslandsanmeldungen für Patente oder Erfinderurkunden, oder §365(a) aller PCT internationalen Anmeldungen, welche wenigstens ein Land ausser den Vereinigten Staaten von Amerika benennen, und habe nachstehend durch ankreuzen sämtliche Auslands- anmeldungen für Patente bzw. Erfinderurkunden oder PCT internationale Anmeldungen angegeben, deren Anmeldetag dem der Anmeldung, für welche Priorität beansprucht wird, vorangeht.

I hereby claim foreign priority under Title 35, United States Code, §119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed

Prior Foreign Applications
(Frühere ausländische Anmeldungen)

(Number) (Nummer)	(Country) (Land)	(Day/Month/Year Filed) (Tag/Monat/Jahr der Anmeldung)	Priority Not Claimed / Priorität nicht beansprucht
197 28 682.8	Germany	04 July 1997	☐
197 32 462.2	Germany	28 July 1997	☐

(see attached sheet)

Ich beanspruche hiermit Prioritätsvorteile unter Title 35, US-Code, § 119(e) aller US-Hilfsanmeldungen wie unten aufgezählt.

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below

(Application No.) (Aktenzeichen)	(Filing Date) (Anmeldetag)

Ich beanspruche hiermit die mir unter Title 35, US-Code, § 120 zustehenden Vorteile aller unten aufgeführten US-Patentanmeldungen bzw. § 365(c) aller PCT internationalen Anmeldungen, welche die Vereinigten Staaten von Amerika benennen, und erkenne, insofern der Gegenstand eines jeden früheren Anspruchs dieser Patentanmeldung nicht in einer US-Patentanmeldung, bzw. PCT internationalen Anmeldung in in einer gemäß dem ersten Absatz von Title 35, US-Code, § 112 vorgeschriebenen Art und Weise offenbart wurde, meine Pflicht zur Offenbarung jeglicher Informationen an, die zur Prüfung der Patentfähigkeit in Einklang mit Title 37, Code of Federal Regulations, § 1.56 von Belang sind und die im Zeitraum zwischen dem Anmeldetag der früheren Patentanmeldung und dem nationalen oder im Rahmen des Vertrags über die Zusammenarbeit auf dem Gebiet des Patentwesen (PCT) gültigen internationalen Anmeldetags bekannt geworden sind.

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(Application No.) (Aktenzeichen)	(Filing Date) (Anmeldetag)	(Status) (patented, pending, abandoned) (Status) (patentiert, schwebend, aufgegeben)
PCT/EP98/03349	4 June 1998	published

Ich erkläre hiermit, daß alle in der vorliegenden Erklärung von mir gemachten Angaben nach bestem Wissen und Gewissen der Wahrheit entsprechen, und ferner daß ich diese eidesstattliche Erklärung in Kenntnis dessen ablege, daß wissentlich und vorsätzlich falsche Angaben oder dergleichen gemäß § 1001, Title 18 des US-Code strafbar sind und mit Geldstrafe und/oder Gefängnis bestraft werden können und daß derartige wissentlich und vorsätzlich falsche Angaben die Rechtswirksamkeit der vorliegenden Patentanmeldung oder eines aufgrund deren erteilten Patentes gefährden können

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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VERTRETUNGSVOLMACHT: Als benannter Erfinder beauftrage ich hiermit den (die) nachstehend aufgeführten Patentanwalt (Patentanwalte) und/oder Vertreter mit der Verfolgung der vorliegenden Patentanmeldung sowie mit der Abwicklung aller damit verbundenen Angelegenheiten vor dem US-Patent-und Markenamt. *(Name(n) und Registrationsnummer(n) auflisten)* (2)	POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: *(list name and registration number)* Richard H. Tushin, Reg. No. 27,297 Lawrence R. Radanovic, Reg. No. 23,077
Postanschrift:	Send Correspondence to: DYKEMA GOSSETT PLLC Franklin Square, Third Floor West, 1300 I St., N.W., Washington, D.C. 20005-3353
Telefonische Auskünfte *(Name und Telefonnummer)*	Direct Telephone Calls to: *(name and telephone number)* Richard H. Tushin (202) 622-8680

Vor- und Zuname des einzigen oder ersten Erfinders	Full name of sole or first inventor SAUER, Sarolf
Unterschrift des Erfinders Datum	Inventor's signature Date
Wohnsitz	Residence Lainzer Str. 64, A-1130 Wien, Austria
Staatsangehörigkeit	Citizenship Austria
Postanschrift	Post Office Address Same as above
Vor- und Zuname des zweiten Miterfinders (falls zutreffend) 1-00	Full name of second joint inventor, if any KLEPSCH, Christian
Unterschrift des zweiten Erfinders Datum	Second Inventor's signature Date Christian Klepsch 1. 9. 2001
Wohnsitz	Residence A-5201 Koppeltorstrasse 8, Seekirchen, Austria ATX
Staatsangehörigkeit	Citizenship Austria
Postanschrift	Post Office Address Same as above

(Im Falle dritter und weiterer Miterfinder Miterfinder sind die entsprechenden Informationen und Unterschriften hinzuzufügen.)

(Supply similar information and signature for third and subsequent joint inventors.)

Prior Foreign Applications			Priority Not Claimed
197 32 461.4	Germany	28 July 1997	
197 40 160.0	Germany	12 September 1997	
197 44 876 3	Germany	10 October 1997	
197 40 163.5	Germany	12 September 1997	

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS (37 CFR 1.9(f) AND 1.27 (c)) - SMALL BUSINESS CONCERN	Docket No. A-6865

Serial No.	Filing Date	Patent No.	Issue Date
09/446,128	December 28, 1999		

Applicant/ Patentee: **Sauer, Sarolf and Klepsch, Christian**

Invention: **PROCESS FOR FURTHER PROCESSING OF SMALL GLASS PARTICLES**

I hereby declare that I am:

- ☐ the owner of the small business concern identified below:
- ☒ an official of the small business concern empowered to act on behalf of the concern identified below:

NAME OF CONCERN: **Starshine Glastechnologie GmbH**
ADDRESS OF CONCERN: **Weinbach 14, A-5351 Aigen-Voglhub, Austria**

I hereby declare that the above-identified small business concern qualifies as a small business concern as defined in 13 CFR 121.3-18, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees under Section 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the above identified invention described in:

- ☐ the specification filed herewith with title as listed above.
- ☒ the application identified above.
- ☐ the patent identified above.

If the rights held by the above-identified small business concern are not exclusive, each individual, concern or organization having rights to the invention is listed on the next page and no rights to the invention are held by any person, other than the inventor, who could not qualify as an independent inventor under 37 CFR 1.9(c) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

Each person, concern or organization to which I have assigned, granted, conveyed, or licensed or am under an obligation under contract or law to assign, grant, convey, or license any rights in the invention is listed below:

☒ no such person, concern or organization exists.
☐ each such person, concern or organization is listed below.

FULL NAME ______________________
ADDRESS ______________________
☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

FULL NAME ______________________
ADDRESS ______________________
☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

FULL NAME ______________________
ADDRESS ______________________
☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

FULL NAME ______________________
ADDRESS ______________________
☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING: ______________________
TITLE OF PERSON SIGNING
OTHER THAN OWNER: ______________________
ADDRESS OF PERSON SIGNING:

SIGNATURE: ______________________ DATE: 10.3.00